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Cement chemistry-performance relationships from time resolved *in-situ* and *ex-situ* studies
2007 activities

PI

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Contents

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Abstract

Portland cement is used in large quantities to "grout" oil wells. Oil well cement is placed between a metal liner and the walls of the bore hole. It provides support for the liner and a seal to prevent the migration of gas etc. along the outside of the liner. The cement has to perform under demanding conditions as high temperatures and pressures, and chemically aggressive environments, are often encountered. It is very important that the cement slurry does not prematurely set while it is being pumped, as this would block the well. Additionally, the cement must set in a short time so that large amounts of money are not lost due to delays, and the transition time for the slurry should be short so that problems with gas percolation into the cement are avoided. Long-term performance is also of great concern. If the cement does not provide a good seal, gas can migrate to the surface and lead to very significant safety and environmental problems. Fully understanding the chemistry and materials engineering behind oil well cement setting and aging is a major economic issue and a very important issue for the health of our environment.

The setting characteristics of oil well cements are in practice controlled by the addition of retarders, accelerators and other additives such anti-gelation agents and silica flour. Different additives, or combinations of them, are needed depending upon the temperature of the well. However, the effect of these additives on the hydration chemistry of the cement is not definitively established. We will examine the hydration of API class A, G and H cements under a range of conditions (temperature and pressure) that are relevant to Halliburton's business in the presence of various accelerators, retarders, anti-gelation agents and strength retrogression control agents using a combination of methods. The methods to be employed include, in-situ diffraction and x-ray small angle scattering using synchrotron x-ray sources, ex-situ diffraction, ultrasound transit times, and rheological measurements. These measurements will be carried out in collaboration with personnel from Halliburton Energy Services. From the body of data that is acquired, we will be able to better establish the cement's hydration pathway in the presence of the additives and correlate this hydration chemistry with the time evolution of physical properties. These correlations will be used to 1) enhance our confidence that currently used additives will have no unintended consequences, 2) reduce the uncertainty that is sometimes associated with current generation additives, 3) reduce the need for empirical testing of slurry compositions, and 4) provide a technical basis for the development of new additives and hence facilitate the rational development of new products.

Cement chemistry-performance relationships from time resolved *in-situ* and *ex-situ* studies: A basis for new and improved products 2007 activities

Scientific purpose

Portland cement is used in large quantities to "grout" oil wells. Oil well cement is placed between a metal liner and the walls of the bore hole. It provides support for the liner and a seal to prevent the migration of gas etc. along the outside of the liner. The cement has to perform under demanding conditions as high temperatures and pressures, and chemically aggressive environments, are often encountered. It is very important that the cement slurry does not prematurely set while it is being pumped, as this would block the well. Additionally, the cement must set in a short time so that large amounts of money are not lost due to delays, and the transition time for the slurry should be short so that problems with gas percolation into the cement are avoided. Long-term performance is also of great concern. If the cement does not provide a good seal, gas can migrate to the surface and lead to very significant safety and environmental problems. Fully understanding the chemistry and materials engineering behind oil well cement setting and aging is a major economic issue and a very important issue for the health of our environment.

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Prior cement hydration work for Halliburton

In our 2003 pilot study of retarder action in oil well cements we made use of time resolved synchrotron x-ray diffraction to examine cement hydration at elevated temperatures under autogenous pressure in the presence of several retarders. These measurements illustrated the power of *in-situ* time resolved work. We observed an intermediate phase that was not anticipated prior to the experiments, discovered that different retarders effected the formation of the hydration product ettringite in different ways (HR25 suppresses the formation of ettringite unlike the other retarders examined) and found that dramatic rheological changes in the cement slurry seemed to correlate with chemical changes that could be potentially targeted by appropriate additives. The results from this study have been summarized in a report to Halliburton and published in the open literature.[1]

Figure 1. Sapphire high pressure cell mounted at the DND CAT BM5D beam line of the Advanced Photon Source for real time x-ray diffraction studies (November 2004). Cement slurries are placed in a 1/8" OD sapphire tube that is mounted horizontally and surrounded by an aluminum heater block. This apparatus has been used at pressures of up to ~ 7,500 psi and temperatures of up to ~200 °C to study cement hydration chemistry in real time.

In 2004, we started by examining the hydration of API class A cement in the presence of calcium chloride and sodium sulfate. This work revealed that under some conditions the use of these additives results in the formation of phases that do not form without these additives. We also discovered an unanticipated time / $CaCl_2$ concentration dependence in the formation of calcium hydroxide that may be of relevance to long term strength development in the cement. In August 2004, we performed a more detailed study of the hydration of Class H cement with retarders under autogenous pressure in the temperature range 90 - 120 °C. Corresponding rheological data were recorded. In November/December 2004, studies of cement hydration at elevated temperatures and high external pressures (up to 7500 psi in these preliminary measurements) were begun. The sapphire high pressure cell that was constructed for these measurements (see Figure 1) performed quite well enabling us to collect high quality diffraction patterns in real time as the cement slurries hydrated at high P and T. Additionally, it was demonstrated that stainless steel tubing could be used for real time high pressure studies when very high energy x-rays were available. A paper describing the high pressure cell design and experimental methodology has been published.[2] These measurements indicated that pressure played a role in the production of portlandite and Jaffeite in the retarded class H slurries, but that the magnitude of the pressure effects as seen by *in-situ* diffraction depended on the temperature of the slurry and the retarder that was being used.

In early 2005, measurements were performed on class H slurries accelerated with $CaCl_2$, so that we could compare the effects of this accelerator on class A (2004 measurements) and class H cements. A paper on our $CaCl_2$ work has been submitted for publication.[3] The hydration of class H slurries containing a variety of different silica sources as strength retrogression control agents was also examined under autogenous pressure and, later in the year, at both ~1000 and 7000 psi using the sapphire high pressure cell. These experiments showed that while tobermorite is typically formed in these slurries, silica fume can significantly delay the hydration of C_3S and the formation of tobermorite. They also showed that while the hydration of most slurries did not show a strong pressure dependence, some showed a dramatic dependence on pressure. The origin of this pronounced pressure dependence for some slurry compositions is not yet understood. A manuscript on this added silica work has been prepared for publication and is currently under internal review at Halliburton.[4] In December 2005, a further series of high pressure measurements on Class H slurries in the presence of retarders was undertaken to obtain a more complete picture of how slurry temperature and retarder type alter the slurries' sensitivity to pressure. The results from this work are now being prepared for publication. A document providing an overview of all of the work up until this point had been submitted as a conference proceedings paper for the International Cement Chemistry Conference 2007.[5]

In March 2006, we undertook a study of class G cement hydration in the presence of various additives, including the anti gel additive FDP-C750-04, using a combination of *in-situ* diffraction and rheology measurements. This work delivered high quality data, but their complete evaluation is still underway. In August 2006, a series of experiments on high alumina based cement (Thermalock) slurries was performed. Our apparatus for high pressure *in-situ* diffraction studies was significantly upgraded in 2006, so that pressure of 15,000 psi could be attained (the prior equipment was limited to ~8,000 psi). However, our initial source of sapphire tubing for use with the upgraded cell provided material that contained inclusions and these tubes suffered from a very high failure rate. We are pursuing an alternative source of sapphire pressure tubes for use at 15,000 psi, and working with personnel at Halliburton to develop a steel pressure tube design that is compatible with our existing equipment and usable to 15,000 psi for *in-situ* x-ray studies (we have previously used our apparatus at up to ~7,000 psi for x-ray studies with steel tubes). In 2006, we have developed an ultrasound testing capability at Georgia Tech. Initially, we have confined our measurements to compression wave propagation in slurries at room temperature. We will perform initial simultaneous *in-situ* diffraction and ultrasound measurements in November/December 2006.

In 2007 we will continue to develop our ultrasound and high pressure testing capabilities. We will further develop our ultrasound testing capabilities to include both compression and shear wave measurement, so that we can follow the development of slurry elastic (mechanical) properties as a function of time while recording diffraction data. This should be particularly useful for studies of gelation, and in combination of with *in-situ* X-ray methods, we should get additional insight into the relationship between chemistry and mechanical property development. We also plan to perform some x-ray small angle scattering test measurements in 2007, as this technique can provide information on nanostructure (gel surface area development) that is likely to be important in understanding our elastic property measurements. We will perform one further set of high pressure measurements in 2007, at pressures up to 15,000 psi. The goal of this study is to examine a small number slurries at several pressures between 0 and 15,000 psi and look at the pressure dependence of hydration in detail.

General technical objectives for 2007 work

1) Explore the effect of accelerators, anti-gelation agents, retarders and strength retrogression additives on cement chemistry and look for the correlations between this chemistry and rheological/mechanical properties.

2) Identify the mechanisms by which the additives operate. Use this data to better predict pumping times, and better understand both product variability and performance.

3) Further examine the effect of pressure on cement chemistry as it is known that this variable plays a big role in cement slurry rheology.

4) Examine the use of anti-gelation agents in order to develop an understanding of how they modify cement chemistry.

6) Further develop and test x-ray cells suitable for the simultaneous measurement of ultrasound transit times so that we can simultaneously follow cement chemistry as seen by diffraction and/or SAXS (small angle x-ray scattering) and mechanical property development as seen by the ultrasound measurements. The correlation of physical properties and chemistry will be greatly facilitated by simultaneous measurements, as uncertainties, such as slightly different temperatures or mixing procedures, arising from two separate sets of measurements would be eliminated.

Description of the work to be performed

General description

In-situ time resolved diffraction studies of cement chemistry will be performed by the Georgia Tech. team. These data will be matched with rheological measurements from Halliburton Energy Services so that cement chemistry property relationships can be developed. The *in-situ* studies will include experiments performed at the Advanced Photon Source (DOE synchrotron facility). The *in-situ* measurements will be used to examine cement chemistry in the time range of 10 minutes to 1 day. The *in-situ* synchrotron studies will employ sample environment that we have already developed and tested, such as sealed Kapton or polybenzimidazole containers for diffraction experiments under autogeneous pressure and a heated sample cell based on a single crystal sapphire tube for experiments at pressures of several hundred bar, as well as new cell designs. We will further develop our initial cell design for simultaneous x-ray and ultrasound measurements. We will also examine the possibility of simultaneous small angle X-ray scattering measurements, probing gel nanostructure, and diffraction measurements and/or ultrasound transit times.

Systems to be studied

Cements with accelerators and Anti-gelation agents. The hydration of cement in the presence/absence of anti-gelation agents and or accelerators will be examined by a combination of ultrasound and x-ray scattering. The propagation of both shear and longitudinal waves will be examined so that the elastic moduli for the slurry can be followed as a function of time. The x-ray scattering data will be correlated with the moduli to probe the mechanism(s) by which these agents function. We anticipate focusing on polystyrene sulfonate in the presence of lignosulfonate and/or $CaCl_2$ for the initial measurements. $CaCl_2$ is known to exacerbate problems with gas percolation due to the long time period between the formation of a gel and the development of sufficient strength to prevent gas ingress.

Retarded cements at higher pressures. We will extend our work in this area to include pressures up to ~ 1000 bar. Previously we have only examined samples at up to 500 bar. By going to high pressure we should see stronger pressure effects and be able to assess how the effects that we have already seen vary with pressure. This later point is potentially important as the effects may be nonlinear with pressure.

Systems with added silica at high pressure. In our prior work we found a very strong pressure dependence for some slurries containing added silica, but a weak pressure dependence for other slurries. We will expand the range of composition examined to try and understand why all slurries with similar amounts of added silica do not behave in the same way as one another.

Benefits to Halliburton

The results from the proposed experiments should, ultimately, result in a more rational approach to product development with less empirical testing and hence a cost saving.

Conditions of access to DOE synchrotron facilities

The proposed synchrotron experiments will make use of the Advanced Photon Source (APS) at the Argonne National Laboratory. Access to this DOE facility will be achieved primarily through the General User Program. Access to beam time through the General User Program requires that we agree to disclose the results of the synchrotron experiments. Disclosure must take the form of a report that will appear in the APS annual report book and publications in the open literature detailing any scientifically significant findings. In the event that a synchrotron measurement is needed without public disclosure, it is possible to pay full cost recovery for the synchrotron experiment and maintain confidentiality.

Bibliography

[1] A. C. Jupe, A. P. Wilkinson, K. Luke and G. P. Funkhouser, "Class H Oilwell Cement Hydration at Elevated Temperatures in the Presence of Retarding Agents: An in-situ High Energy X-ray Diffraction Study," *Ind. Eng. Chem. Res.* 44, 5579-5584 (2005).

[2] A. C. Jupe and A. P. Wilkinson, "Sample cell for powder X-ray diffraction at up to 500 bar and 200°C," *Rev. Sci. Inst.* 77, 113901-1 to 4 (2006).

[3] A. C. Jupe, A. P. Wilkinson, K. Luke and G. P. Funkhouser, "Slurry Consistency and In-situ Synchrotron X-ray Diffraction during the Early Hydration of Portland Cements with Calcium Chloride," *J. Am. Ceram. Soc.*, (submitted for publication).

[4] A. C. Jupe, A. P. Wilkinson, K. Luke and G. P. Funkhouser, "Class H cement hydration at 180 °C and high pressure in the presence of added silica," *Cem. Concr. Res.*, (in preparation).

[5] A. C. Jupe, A. P. Wilkinson, K. Luke and G. P. Funkhouser, "The Development and Utility of In-Situ Synchrotron Diffraction for Studying Oil Well Cement Hydration at Elevated Temperatures and Pressure," *Proceedings of the 2007 Internation Conference on Cement Chemistry, Montreal.*, (submitted for publication).

Project budget for 2007

Personnel	Wilkinson one month	$ 10,686
	Jupe twelve months	$ 42,300
Fringe (24.1% of salary)	On all fulltime staff salaries	$ 12,770
Total personnel and Fringe		**$ 65,756**
M+S	Machine shop time, consumable items including sapphire tubes and stainless steel for high pressure experiments. Equipment maintenance.	$ 13,000
		$ 13,000
Travel	Travel to use a total of ~3 weeks of synchrotron time involving two people from GT. $2200/week. Also funds for Jupe and Wilkinson to attend ICCC in July 2007 where they are presenting a paper on their work with Halliburton.	**$ 9,400**
Total direct costs		**$ 88,156**
Overhead (54.6% for industrial contracts)	All none equipment items	**$ 48,133**
Total cost to sponsor		**$ 136,289**